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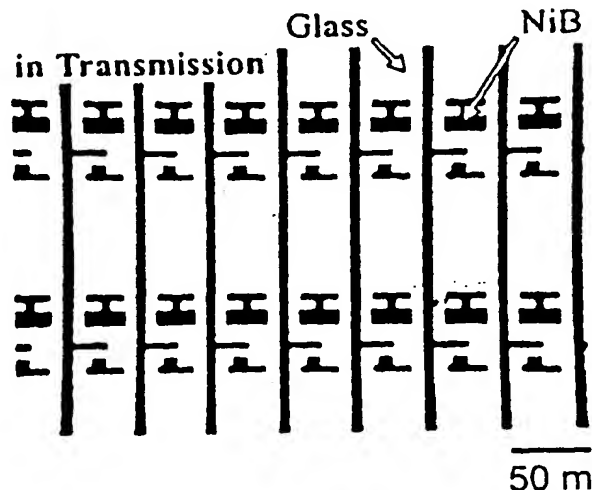
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(54) Title: METHOD FOR ELECTROLESS DEPOSITION AND PATTERNING OF A METAL ON A SUBSTRATE



(57) Abstract: A method for manufacturing a pat-
terned metal layer on a substrate is provided which
comprises the step of electrolessly depositing a blan-
ket metal film of a metal onto a substrate, followed
by subsequently patterning said metal layer by means
of microcontact printing. The deposited metal can be
overplated with another metal, which can be micro-
contact printed to serve as an etch mask.

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D E S C R I P T I O N

Method for Electroless Deposition and Patterning of a Metal on a
Substrate

Field of the Invention

The present invention relates to a method for electroless deposition and patterning of a metal on a substrate. More specifically, the invention relates to such a method wherein the process steps of microcontact printing and electroless deposition are combined.

Background of the Invention, Prior Art

Patterning a metal over a substrate is a common need and important process in modern technology; it is applied, e.g., in microelectronics and display manufacturing. This patterning usually requires the vacuum deposition of a metal over the entire surface of a substrate and its selective removal using photolithography and etching techniques. The vacuum deposition of the metal and the consumption of photoresist constitute considerable cost factors in the fabrication of metallic structures, and limit the size of substrates that can be patterned by this approach.

The technique of electroless deposition (hereinafter ELD) of metals on (insulating) surfaces can provide an alternative to the vacuum deposition of metals on substrates (cf., e.g. "Electroless Plating: Fundamentals and Applications", G.O. Mallory, J.B. Hajdu, Eds.; American Electroplaters and Surface Finishers Society, Orlando, Fl, 1990).

Electroless deposition of metals such as copper, silver, gold,

nickel, rhodium, and cobalt is a process widely used for the production of fine metal patterns in printed circuits. Electroless deposition occurs by an autocatalytic redox process, in which the cation of the metal to be deposited is reduced by a soluble reductant at the surface of the metal features being formed, or at the surface of catalysts used to initiate the deposition. This redox process generally takes place only on surfaces capable of catalyzing it. Noncatalytic surfaces first have to be activated with a metal catalyst such as palladium before the metalization can occur. Selective deposition can be achieved either by the selective deactivation of a catalytic substrate or by the selective activation of a nonreactive surface by a catalyst. Several methods of producing patterned catalysts are known, most of them based on photolithographic techniques. The size of the features produced by electroless deposition of metals can be as small as 0.1 μm .

Microcontact printing can also provide an alternative to the patterning of metals using photolithography.

Microcontact printing (hereinafter μCP) is a technique for forming patterns of organic monolayers with micrometer and submicron lateral dimensions. It offers experimental simplicity and flexibility in forming certain types of patterns by printing molecules from a stamp onto a substrate. So far, most of the prior art relies on the remarkable ability of long chain alkanethiolates to form self-assembled monolayers on, e.g., gold or other metals. These patterns can act as nanometer-thin resists by protecting the supporting metal from corrosion by appropriately formulated etchants, or can allow for the selective placement of fluids on hydrophilic regions of the printed pattern. Patterns of self-assembled monolayers having lateral dimensions that can be less than 1 micrometer can be formed by using a solution of alkanethiols dissolved in ethanol as the "ink", and by printing them on a metal substrate using an elastomeric "stamp". The stamp is fabricated by molding a

silicone elastomer using a master (or mold) prepared using photolithography or using other techniques such as electron-beam lithography. Patterning of the surface of such a stamp is, e.g., disclosed in EP-B-0 784 543.

In Hidber et al., „Microcontact Printing of Palladium Colloids: Micron-Scale Patterning by Electroless Deposition of Copper“, Langmuir, vol. 12, 1996, p1375-1380), a method for forming micron- and submicron-scale patterns of copper on surfaces is disclosed. This method uses μ CP to print colloids that serve as catalysts for the selective electroless deposition of copper. A patterned elastomeric stamp fabricated from poly-(dimethylsiloxane) (hereinafter PDMS) is used to deliver the catalyst (palladium colloids stabilized with tertaalkylammonium bromides and dissolved in toluene) to the surface of a substrate. Electroless deposition of copper on the substrate occurred only where palladium colloids were printed and transferred to the substrate. Electroless deposition catalyzed by the colloids resulted in the formation of metal structures with features having submicron dimensions.

WO 00/79023 A1 discloses methods for electroless deposition of a conductive material on a substrate using a stamp having a patterned surface which is pressed onto the surface of a substrate for printing the substrate and providing a pattern of a catalyst on the substrate on which metal deposition occurs in the course of electroless deposition by immersing the printed substrate in a plating bath.

Thus, these two references have documented how to combine μ CP and ELD. In summary, these approaches involve (i) derivatizing the substrate with chemical functionalities having an affinity for a catalyst for ELD, (ii) inking a micropatterned PDMS stamp with a solution of catalyst, (iii) printing the catalyst on the substrate, and (iv) ELD of a metal over the printed catalytic pattern. In short, this strategy can be referred to as „Print &

ELD". This strategy can vary depending on what exactly is printed on the substrate. Apart from printing the catalyst onto the substrate, it is equally possible to print molecules onto a substrate to enhance the affinity of the catalyst for that substrate. In this variation, the printed substrate must then be immersed into a bath of catalyst to add the catalyst to the printed regions of the substrate. Another variation consists of homogeneously coating a substrate with a layer of catalyst for ELD and of printing molecules to deactivate the catalyst already present on the surface of that substrate. Still another variation can be to homogeneously coat a substrate with a layer of pre-catalyst and to print molecules to this precoated substrate to activate the pre-catalytic particles.

However, the „Print & ELD" strategy and its possible variations show some serious drawbacks. First, chemicals providing adhesion between a catalyst for ELD and glass substrates tend to be self-reactive and cannot be inked easily onto a "classical" PDMS stamp, nor transferred homogeneously onto a substrate. PDMS is a hydrophobic elastomer and a surface treatment of PDMS to render it hydrophilic may also be necessary in such a case.

Next, typical catalysts for ELD such as Pd/Sn colloids are used in highly acidic (usually concentrated hydrochloric acid) solutions because these colloids are usually unstable in other types of solutions. These colloids are catalysts for ELD of many metals and are very active. They are particularly well optimized for ELD but the compatibility of a highly acidic ink with a printing tool is questionable: HCl gas from the ink would corrode a printing tool and the metallic backplane of the stamp, and these vapors would also pose safety problems.

In addition to these drawbacks, no activators (or deactivators) of catalysts for ELD, that can be printed have been identified so far that are compatible with stamps. This excludes using the other approaches to „Print & ELD" mentioned above to combine ELD

and μ CP.

Furthermore, when trying to use an ink for „Print & ELD“, the following questions arise that have not yet been solved: How is the stamp to be inked? How should it be dried? How could a stamp be used repeatedly with only one inking? How should the ink be cleaned from a stamp? How can diffusion of the ink over the substrate be controlled and prevented during printing? How could homogeneous inking of a stamp and transfer of an ink be achieved without variable catalytic activity across large substrates? And, importantly, how can a reasonable process throughput be achieved to render „Print & ELD“ economically attractive to solve the problem of reducing the cost of fabrication of metallic structures on substrates?

Achieving good adhesion between the electroless-deposited metal and its substrate is the most important challenge in ELD. An electroless-deposited metal can lose its adhesion to the substrate in the plating bath during deposition, during the removal of the plated substrate from the ELD bath, during rinsing or drying the freshly plated metal, or later during post-processing or subsequent device-fabrication steps. As a consequence, good adhesion between a deposit and a substrate is always desirable and often the result of optimizing all the details of an ELD process, starting with treating the substrate received from the supplier and post-processing the deposited metal to relieve stress in the materials.

Summary of the Invention

It is therefore an object of the present invention to provide a method for electroless deposition and patterning of a metal on a substrate that combines the process steps of microcontact printing and electroless deposition.

It is still another object of the present invention to provide such a method that allows good adhesion between an electroless-deposited metal and its substrate if one step involves microcontact printing.

These and other objects and advantages are achieved by the method disclosed in claim 1.

Preferred embodiments of the invention are described in the dependent claims.

Brief Description of the Drawings

The invention will be described in more detail hereinafter in connection with the drawings, in which

Fig. 1A is an optical image with the light in reflection, showing a high-quality pattern of lines of NiB alloy on glass patterned according to the invention;

Fig. 1B is an optical image with the light transmitted through the glass substrate corresponding to the image of Fig. 1A;

Fig. 1C is an atomic force microscope image of the pattern according to Figs. 1A and 1B; and

Fig. 2 shows X-ray photoemission spectra obtained on macroscopic areas of NiB and glass resulting from patterning NiB according to the invention.

Detailed Description of the Preferred Embodiment

As has already been mentioned above, the strategy proposed by Hidber et al. and in WO 00/79023 A1 can be referred to as „Print & ELD“.

Another strategy is, according to the present invention, to use ELD to prepare a blanket film of a metal, which can be subsequently patterned by means of microcontact printing. This strategy is called „ELD & Print“. It is important to note that both strategies are not symmetric, i.e. they do not entail simply performing the same steps in a different or reverse order.

The present invention proposes a new combination of the process steps of μ CP and ELD.

Inverting the sequence for performing the printing and the electroless deposition steps solves many of the above-mentioned problems and necessitates, in contrast, a quite new process flow. This inversion compromises the localized ELD of a metal but, instead, the deposited metal can be overplated with another metal, which can be microcontact printed to serve as an etch mask.

In general, the process flow is as follows:

1. Preparing the electrically insulating surface by deposition of a catalyst;
2. Electrolessly depositing a first metal from a solution;
3. Preparing the first metal surface for printing, i.e., annealing, reduction of the surface oxide using forming gas, oxidation in air, cleaning, or depositing additional metal films via electrodeposition or electroless deposition

and prepare the surface of the second metal for microcontact printing;

4. Patterning this surface using μ CP of a suitable ink that acts as an etch barrier in the subsequent etch step; and
5. Etching the metal or metal films in suitable solutions.

The simplest possible approach contains the steps of ELD of Au, μ CP a self-assembled monolayer of alkanethiols on Au and a subsequent selective etch of Au.

Microcontact printing alkanethiols on Au substrates down to a resolution of 1 micrometer is the only application of microcontact printing that is firmly established (c.f., Delamarche et al., J. Phys. Chem. B, vol. 102, 1998, p3324-3334). It may then seem optimal to develop a strategy based on ELD of Au and printing the deposited Au with thiols and etching it for patterning.

This approach is not favorable due to issues such as cost, poor adhesion of Au to the substrate, and, depending on the sought application, semiconductor contamination (by formation of recombination centers (traps) in silicon due to the likely diffusion of Au atoms into adjacent Si layers). Ag may also be used for this application; however, ELD of Ag is difficult to control and typically results in films with poor adhesion to smooth insulating substrates. Ag poses also problems with semiconductor contamination, and Ag is prone to electromigration and corrosion. Cu can also be printed with alkanethiols and etched selectively if one takes into account the oxide present at the surface of this metal and its high sensitivity to certain etchants. As with Au and Ag, the adhesion of plated Cu films on smooth insulating surfaces is limited.

Therefore, another approach is presented, namely ELD of a first

metal followed by deposition of a second metal and printing.

Since a single ELD metal (e.g., Au, Ag, Cu) may not provide desirable properties such as good adhesion and compatibility with μ CP, a multilayer metallization and printing process may be preferred. For example an electrolessly deposited film of Ni, Co, or Pd (or alloys thereof) may be used as a first layer and a second metal layer such as Cu, Ag, or Au (ELD or electroplated) may be used for printing and as an etch barrier. In particular, Ni and Ni alloys (NiB, NiP, NiWP, NiReP, etc.) are excellent candidates for ELD on smooth insulating substrates. Several Ni baths are commercially available that yield plated Ni with good conductivity. In this invention, a glass treatment and a process in general has been developed that improves the adhesion on glass of electroless deposited Ni. Cu is convenient to electroplate, inexpensive, compatible with Ni when it is electroplated, and it can be a good substrate for microcontact printing alkanethiols. The high conductivity of NiB and Cu helps keeping the current density homogeneous during the electroplating step on large samples, which is important to obtain an electroplated mask having a uniform thickness. Printed Cu can be etched selectively to serve as a mask for the underlying Ni. The Cu mask can be easily removed at the end of the process if desired.

A typical flow of an „ELD & Print“ process according to the present invention is as follows:

1. An organic layer having an affinity for a catalyst for ELD is grafted from solution onto a glass substrate.
2. A homogeneous layer of catalytic particles is deposited onto the treated glass from solution and "activation" of the catalyst is done.
3. The substrate is immersed in an ELD bath to deposit the desired metal.

4. The substrate is preferably mounted in a cathode frame and immersed in an electrochemical cell where the sacrificial mask is electroplated. The frame contacts the metal layer on all its periphery to distribute a homogeneous current to this layer and to prevent damaging (scratching) the metal layer in the inner part of the substrate where devices will be fabricated.

5. The mask is selectively protected by microcontact printing a resist (self-assembling monolayer, SAM).

6. The mask and the electroless deposited metal are then selectively etched.

7. The mask is eventually removed entirely.

In the following, an example for the method according to the invention is given. It has to be mentioned that this is an example only and that the present invention is not restricted to the substrates, metallurgy, etch baths, chemicals, etc., mentioned therein, but can be used with other substrates and materials, as will be readily apparent for a skilled worker.

A glass substrate (Corning #1737) is immersed in a solution of N-(2-aminoethyl)-3-aminopropyltrimethoxysilane (hereinafter EDA-Si, from Gelest #SIA0591.0, 0.250 ml in 120 ml of ethanol and 20 ml of water) for 3 min at room temperature. During this step, EDA binds to the glass. The glass is then removed from the grafting bath and rinsed with water and dried. The glass substrate is baked for 10 min on a hot plate at 150 °C or in an oven. This results in a homogeneous, thin grafted layer on the glass that has an affinity for some Pd/Sn colloids. The treated glass can be stored or used immediately after it has cooled.

The glass substrate is then immersed in an acidic Pd/Sn solution

(from Fidelity, article #1018, diluted 50% with HCl conc.) for 30 s to form a homogeneous layer of Pd/Sn catalytic particles for ELD on the grafted glass.

Subsequently, the Pd/Sn glass substrate is rinsed copiously with deionized water and immersed in an "accelerator" solution (from Fidelity, article #1019, 10% in deionized water) for 30 s, then rinsed with deionized water and dried. The thus activated glass substrate is placed on a hot plate at 80 °C. It has to be mentioned that this activating or heating step is optional - in some cases the ELD might work well with a non-activated catalyst.

Now, the pre-heated glass substrate is immersed in a NiB (Shipley, Niposit® 468), prepared as recommended, pH adjusted to 7.2 with ammonia) electroless plating bath operated at 60 °C, with no stirring, to deposit NiB at a rate of about 20-30 nm min⁻¹. The thickness of the ELD NiB film may be controlled by the deposition rate and immersion time.

Subsequently, the glass with a thin (about 50 to 400 nm) NiB film is placed on a hot plate at 150 °C for 10 min to improve the adhesion between the Ni deposit and the glass substrate.

Following this step, a pyrophosphate Cu bath is used to electroplate a thin layer (50 nm) of Cu onto the NiB deposit: 1.1 g of CuSO₄·5H₂O, 3.0 g of Na₄P₂O₇ and 20.0 mg of NaH₂PO₄ are dissolved in 120 ml of deionized water. This bath has a pH of about 9 and is used at 30 °C. The native oxide of Ni typically present on electroless deposited NiB is etched prior to electroplating by immersing the NiB-covered samples in a 0.3 M HCl solution and rinsing them with deionized water. Removing NiO_x is not strictly necessary but provides better adhesion between Ni and Cu.

Electroplating of Cu is done with a potentiostat, model 263A (sold by EG&G) operating at a potential fixed between -0.7 and

-1.0 V (against a Ag/AgCl reference electrode), with a platinized titanium grid (30 cm², samples with larger areas require larger electrodes) as the counterelectrode. Monitoring the current during the plating indicates the rate of Cu deposition and its thickness (0.15 Ccm⁻² for 50 nm of Cu).

The Cu-covered substrates are immersed in a 0.1 M HCl solution for 10 s to remove copper-oxide from the surface, rinsed with deionized water and dried before printing to ensure the formation of a homogeneous and dense protective monolayer during the printing step.

Now, a micropatterned stamp made of PDMS (Sylgard® 184 from Dow Corning) is first inked with a 0.2 mM solution of eicosanethiol (ECT, supplied by Robinson Brothers Limited, article #SV109/4) in ethanol, dried and used to print the electroplated Cu for 20 s, which results in the formation of a monolayer in the regions of contact.

The nonprinted Cu is etched at room temperature in a 0.025 M solution of KCN (in deionized water, buffered at pH 12) with moderate stirring (etch rate about 50 nm of Cu per min). No etch of the NiB deposit during this step was observed.

Subsequently, the NiB is etched in 1 M H₂SO₄ at room temperature with moderate stirring (etch rate about 5-10 nm of NiB per min, this etch rate also depends on the geometry of the pattern) for 20 min. The selectivity of this etch is very high if the Cu mask is still protected by the thiol monolayer; the thiol monolayer on the Cu is removed only later for this reason.

Now the sample is immersed in a water solution containing KOH and 10% of H₂O₂ (pH 14) for 20 min to remove all organic layers (ECT monolayer on copper and EDA grafted layer on the glass). The Pd/Sn catalyst present on the glass where NiB has been etched can also be removed during this step by underetching Sn, the EDA

graft and minute quantities of glass. The electroplated Cu starts equally to be etched during this step, although at a very low rate. This step can be important if the areas left in between the NiB must be well transparent to light or electrically insulated because some Pd/Sn left in these regions could block some light or conduct some current between adjacent, proximal NiB structures.

All remaining Cu is then etched within 2 min in a 0.025 M solution of KCN in water (buffered at pH 12).

The resulting Ni pattern on the glass is again immersed in a solution containing KOH/10% H₂O₂ for a short period of time (<5 min), and washed with a 0.3 M solution of HCl for 2 min. Rinsing with water and drying completes this procedure.

The last two steps are optional. Keeping the sacrificial mask might not be a problem depending on the application, and removing the organic layer and catalyst might as well not be necessary depending on the chosen application.

The optical image in reflection (Fig. 1A) reveals a high-quality pattern of lines of NiB on glass patterned as presented in the example. The corresponding image in transmission (Fig. 1B) emphasizes the possibility of patterning light-absorbing structures on glass with the method according to the invention. Finally, the atomic force microscope image (Fig. 1C) obtained over the edge of one line reveals the good resolution and contrast of this pattern.

The X-ray photoemission spectra shown in Fig. 2 were obtained on macroscopic areas of NiB and glass resulting from patterning NiB as presented in the example. The high level of control over the etch chemistry in this example leads to a glass surface free of metal (Cu, Ni, Pd/Sn), whereas the Ni part of the sample is free of Cu and covered with a thin nickel oxide layer.

Electroless deposition of a metal onto a substrate is a method that must be established in all its details for each case. Beyond the above-mentioned examples, the invention can be extended to:

- several types of substrates (different types of glass, ceramics, oxidized surfaces, Si/SiO₂, indium-tin-oxide, indium-zirconium-oxide, tantalum oxide, aluminum oxide, etc.)
- several types of electroless-deposited first metal layers, e.g., Ni, NiB, NiP, NiWP, Co, CoWP, CoP, Pd, etc.
- several types of electroplated masks, e.g., Au, Cu, and Ag
- alkanethiols showing selective protection for the mask and which are compatible with PDMS micropatterned stamps.

C L A I M S

1. Method for manufacturing a patterned metal layer on a substrate, said method comprising the steps of:
 - a) preconditioning said substrate by grafting an organic layer on said substrate;
 - b) depositing a catalyst layer on said preconditioned substrate;
 - c) depositing a metal layer on said catalyst layer by electroless deposition techniques;
 - d) depositing a sacrificial mask on said metal layer;
 - e) depositing a patterned etch-protection layer on said sacrificial mask using microcontact printing;
 - f) etching away said sacrificial mask in the free areas of said patterned etch-protection layer; and
 - g) etching away said electroless deposited metal layer in the areas free of said sacrificial layer.
2. Method according to claim 1, characterized in that it additionally comprises the step of activating said catalyst layer for electroless deposition after step b).
3. Method according to claim 1 or 2, characterized in that it additionally comprises the step of etching away the remainder of said sacrificial layer.
4. Method according to any one of claims 1 to 3, characterized in that it additionally comprises the step of etching away said grafted organic layer and said catalyst layer.
5. Method according to any one of the preceding claims, characterized in that said organic layer is N-(2-aminoethyl)-3-aminopropyltri-methoxysilane (EDA).

6. Method according to any one of the preceding claims, characterized in that said step of depositing said catalyst layer is accomplished by immersing said substrate into a solution containing catalytic particles.
7. Method according to claim 6, characterized in that said catalytic particles comprise Pd/Sn.
8. Method according to claim 2, characterized in that said activating step is accomplished by immersing said substrate into an accelerator solution.
9. Method according to claim 8, characterized in that said accelerator solution comprises HBF_4 .
10. Method according to any one of the preceding claims, characterized in that said sacrificial mask comprises copper.
11. Method according to claim 10, characterized in that said sacrificial mask is deposited by electroplating.
12. Method according to any one of the preceding claims, characterized in that said etch-protection layer is applied by printing a self-assembled monolayer (SAM) of eicosanethiol by means of a micropatterned stamp.
13. Method according to claim 12, characterized in that said micropatterned stamp is a poly(dimethylsiloxane) (PDMS) stamp.
14. Method according to any one of the preceding claims, characterized in that said step of etching away said sacrificial mask is done with a KCN/oxygen based etching bath.

15. Method according to any one of the preceding claims, characterized in that said step of etching away said metal layer is done with an aqueous solution of H_2SO_4 .
16. Method according to claim 3, characterized in that said step of etching away the remainder of said sacrificial layer is done with KCN.
17. Method according to claim 4, characterized in that said step of etching away said organic layer and said catalyst layer is done with an aqueous mixture of KOH and H_2O_2 .
18. Method according to any one of the preceding claims, characterized in that said substrate is selected from the group consisting of glass, ceramics, oxidized surfaces, Si/SiO₂, and the like.
19. Method according to any one of the preceding claims, characterized in that said electroless deposited metal layer is selected from the group consisting of Ni, NiB, NiP, NiWP, Co, CoWP, CoP, Pd, and the like.
20. Method according to claim 19, characterized in that said metal layer deposited on said catalyst layer comprises an alloy of Ni and B.
21. Method according to any one of the preceding claims, characterized in that said second metal layer is selected from the group consisting of Au, Cu and Ag.
22. Method according to any one of the preceding claims, characterized in that said micropatterned stamp is inked with an alkanethiol.
23. Method according to claim 22, characterized in that said alkanethiol is eicosanethiol.

24. Method according to any one of the preceding claims, characterized in that said etch of said sacrificial mask is performed by etchants being selective for said mask.
25. Method according to any one of the preceding claims, characterized in that said metal layer is etched using any etch chemistry being selective for said sacrificial mask.
26. Method according to any one of the preceding claims, characterized in that a cathode frame is used to electroplate said sacrificial mask.
27. Method according to claim 26, characterized in that said frame contacts said metal layer on all its periphery.

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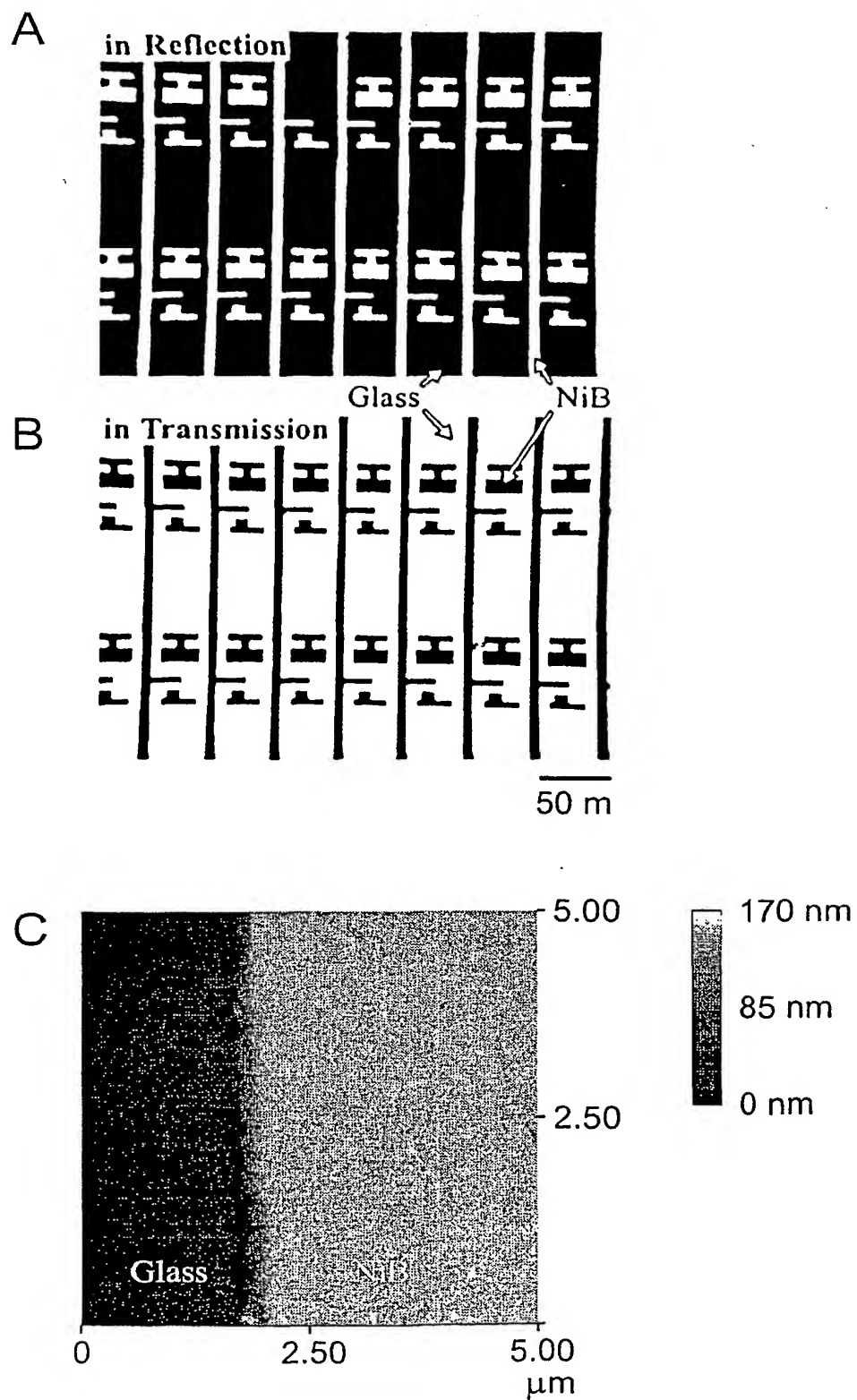


Fig. 1

2/2

XPS signals

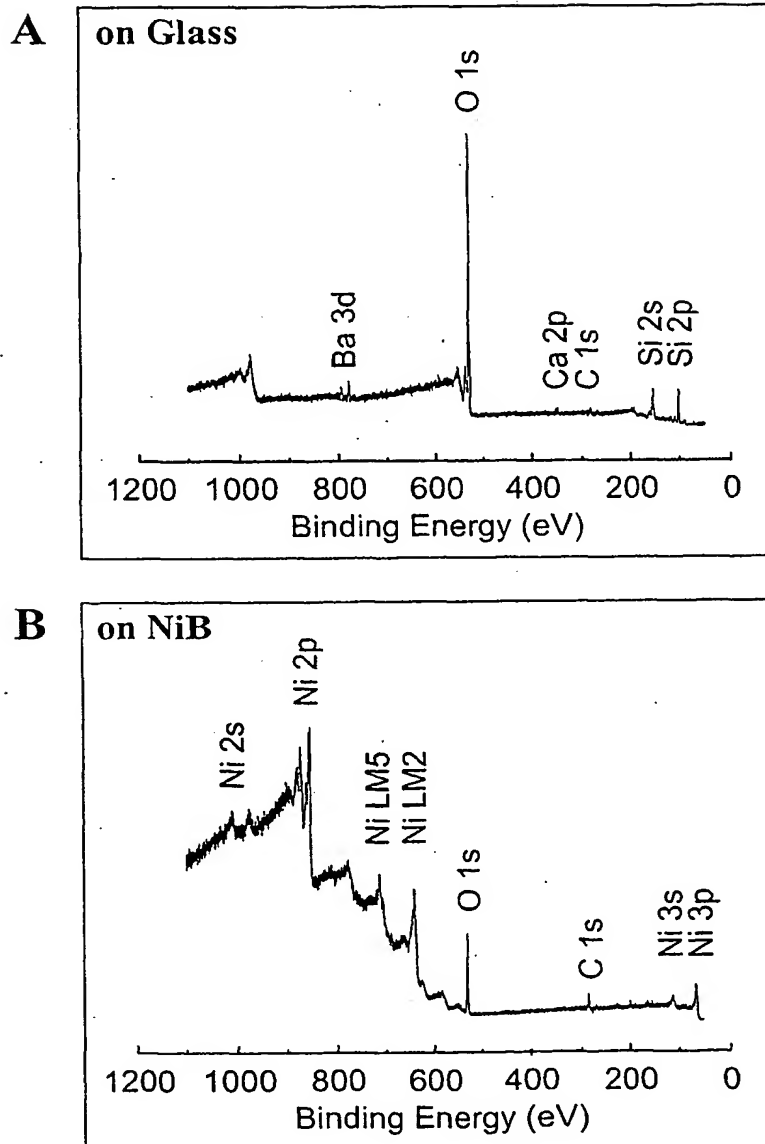


Fig. 2

INTERNATIONAL SEARCH REPORT

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A. CLASSIFICATION OF SUBJECT MATTER

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According to International Patent Classification (IPC) or to both national classification and IPC

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IPC 7 H05K H01L C23F C23C

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Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

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C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WD 00 79023 A (INTERNATIONAL BUSINESS MACHINES CORP.) 28 December 2000 (2000-12-28) cited in the application the whole document	1,4,6, 12,13, 18,22
A	XIA Y ET AL: "Use of electroless silver as the substrate in microcontact printing of alkanethiols and its application in microfabrication" LANGMUIR; LANGMUIR JAN 20 1998 ACS, WASHINGTON, DC, USA, vol. 14, no. 2, 20 January 1998 (1998-01-20), pages 363-371, XP002201958 abstract	1,12,13, 18,21,22

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INTERNATIONAL SEARCH REPORT

Int. Patent Application No

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